Ring Expansion of Diazo-Functionalized 4-Hydroxycyclobutenone: Catalytic Ring Opening and Recyclization to 2(5*H*)-Furanone/Cyclopentenedione and Thermal 4π−8π Electrocyclic Ring Opening−Closure to Diazepinedione

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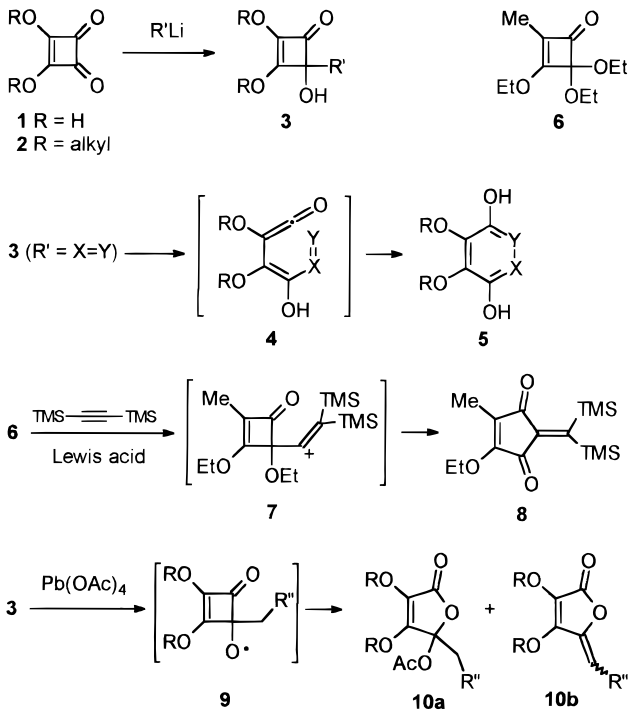
The acid-catalyzed and Rh-catalyzed (also photolyzed) decomposition of 4-hydroxycyclobutenones with a diazo group at C-4 gave 2(5*H*)-furanone and/or cyclopentene-1,3-dione via an α-carbocation intermediate and a carbenoid (carbene) intermediate, respectively. Thermal rearrangement of some of these compounds led to the formation of diazepinediones without the extrusion of nitrogen through tandem 4π electrocyclic ring opening and 8π electrocyclic ring closure processes.

Squaric acid (**1**) continues to attract attention in organic synthesis as a useful C_4-synthon with a four-membered ring strain to drive reactions.[1] Synthesis using **1** starts with the nucleophilic addition of a functional group to cyclobutenedione (**2** → **3**), and the resulting 4-hydroxycyclobutenones **3** are subjected to various ring-transformation reactions (e.g., Scheme 1). Most of these reactions involve tandem electrocyclic rearrangements. The relief of ring strain by 4π ring opening to vinylketene is an initial step,[2] and this is followed by 6π ring closure with the participation of an unsaturated addend, to give polysubstituted six-membered cyclic compounds (**4** → **5**).[3] Paquette and co-workers recently developed an 8π ring closure process for the bisadduct of vinylic carbanions to polyquinanes, which raises new possibilities for the synthetic application of **1**.[4] Alternative ring transformations rely on a 1,2-acyl shift induced by reactive intermediates[5] or transition metal catalysts.[6] These reactions give rise to five-membered rings including 4-cyclopentene-1,3-diones and 2(5*H*)-furanones. Cationic rearrangement has been used to synthesize dimethylgloiosiphone A using such a cyclopentenedione as a key intermediate.[5d] In our laboratory, the Lewis acid-catalyzed reaction of alkynylsilanes with cyclobutenedione monoacetal **6** obtained from **1** was found to involve a new 1,2-silyl shift on the triple bond to generate an α-vinyl cation, which induced ring-expansion to 2-alkylidene-4-cyclopentene-1,3-dione (**7** → **8**).[5f] The oxy-radical generated by the action of $Pb(OAc)_4$ induced β-scission, which was followed by 5-endo-trig cyclization to 2(5*H*)-furanones (**9** → **10**).[5c]

Scheme 1



Regarding the above ring transformations, we have been interested in 4-hydroxycyclobutenones functionalized with a diazo group at the C-4 side chain. This functionality can serve as a carbene and carbocation source and as an unsaturated moiety. The starting diazo-functionalized 4-hydroxycyclobutenones **12a**−**e** were prepared by adding lithium enolates of diazoacetates and a

(1) (a) Schmidt, A. H. *Synthesis* **1980**, 961. (b) Liebeskind, L. S. *Tetrahedron* **1989**, *45*, 3053. (c) Moore, H. W.; Yerxa, B. R. *Chemtracts Org. Chem.* **1992**, *5*, 273. (d) Ohno, M.; Yamamoto, Y.; Eguchi, S. *J. Synth. Org. Chem., Jpn.* **1997**, *55*, 785.

(2) For a theoretical study, see (a) Niwayama, S.; Kallel, E. A.; Sheu, C.; Houk, K. N. *J. Org. Chem.* **1996**, *61*, 2517. (b) Niwayama, S.; Kallel, E. A.; Spellmeyer, D. C.; Sheu, C.; Houk, K. N. *J. Org. Chem.* **1996**, *61*, 2813.

(3) For recent examples, see: (a) Sun. L.; Liebeskind, L. S. *J. Org. Chem.* **1995**, *60*, 8194. (b) Xiong, Y.; Xia, H.; Moore, H. W. *J. Org. Chem.* **1995**, *60*, 6460. (c) Xiong, Y.; Moore, H. W. *J. Org. Chem.* **1996**, *61*, 9168. (d) Tomooka, C. S.; Liu, H.; Moore, H. W. *J. Org. Chem.* **1996**, *61*, 6009. (e) Sun, L.; Liebeskind, L. S. *Tetrahedron Lett.* **1997**, *38*, 3663. (f) Onofrey, T. J.; Gomez, D.; Winters, M.; Moore, H. W. *J. Org. Chem.* **1997**, *62*, 5658.

(4) Paquette, L. A.; Kuo, L. H.; Doyon, J. *J. Am. Chem. Soc.* **1997**, *119*, 3038 and refs cited therein.

(5) (a) Sun. L.; Liebeskind, L. S. *J. Org. Chem.* **1994**, *59*, 6856. (b) Yamamoto, Y.; Ohno, M.; Eguchi, S. *Tetrahedron Lett.* **1995**, *31*, 5539. (c) Yamamoto, Y.; Ohno, M.; Eguchi, S. *J. Am. Chem. Soc.* **1995**, *117*, 9653. (d) Paquette, L. A.; Sturino, C. F.; Dousso, P. *J. Am. Chem. Soc.* **1996**, *118*, 9456. (e) Yamamoto, Y.; Ohno, M.; Eguchi, S. *J. Org. Chem.* **1996**, *61*, 9246. (f) Yamamoto, Y.; Noda, M.; Ohno, M.; Eguchi, S. *J. Org. Chem.* **1997**, *62*, 1292.

(6) (a) Liebeskind, L. S.; Chidambaram, R. *J. Am. Chem. Soc.* **1987**, *109*, 5025. (b) Liebeskind, L. S.; Mitchell, D.; Foster, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 7908. (c) Mitchell, D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 291. (d) Zora, M.; Herndon, J. W. *J. Org. Chem.* **1994**, *59*, 699. (e) Liebeskind, L. S.; Bombrun, A. *J. Org. Chem.* **1994**, *59*, 1149.

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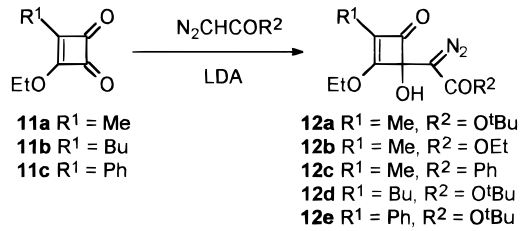
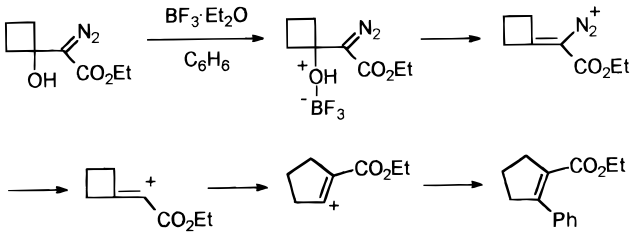
Scheme 2



11a R^1 = Me
11b R^1 = Bu
11c R^1 = Ph

12a R^1 = Me, R^2 = O^{t}Bu
12b R^1 = Me, R^2 = OEt
12c R^1 = Me, R^2 = Ph
12d R^1 = Bu, R^2 = O^{t}Bu
12e R^1 = Ph, R^2 = O^{t}Bu

Scheme 3



diazoketone at −78 °C to cyclobutenedione **11**, which was derived from **1** (Scheme 2).[7]

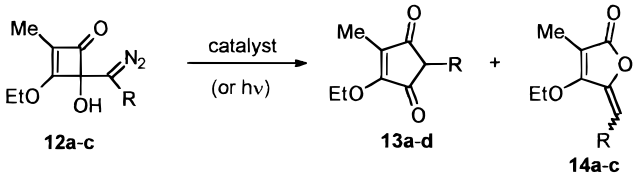
First, the catalyzed decomposition of the three diazo compounds **12a**−**c** was examined. Padwa and co-workers recently reported the prototypical reaction of related diazo-functionalized hydroxycyclobutanes with $BF_3{\cdot}OEt_2$ as a catalyst.[8] In this case, ring expansion to a five-membered ring was explained by a 1,2-methylene shift via a vinyl cation intermediate (Scheme 3).

Thus, α-diazo-α-cyclobutenyl acetate **12a** was allowed to react with this catalyst, and the expected decomposition took place smoothly at 0 °C within 30 min (Table 1, entry 1). After workup and chromatographic separation, three products were obtained, albeit in low yields. One of them was believed to be 1,2-acyl-shifted 4-cyclopentene-1,3-dione **13d** based on spectroscopic examination. The MS molecular ion peak at *m*/*z* 154 reflected the loss of N_2, CO_2, and CH_2CMe_2 from the molecule. ^{1}H NMR (only ethoxy, methyl, and methylene signals at δ 1.40 and 4.69, 1.94, and 2.91, respectively) and ^{13}C NMR (ring carbon signals at δ 42.2, 137.4, 166.7, 196.0, and 197.2 with required signals due to substituents) were compatible with the assigned structure. Ring expansion took place with concomitant fragmentation of the primarily formed *tert*-butyl ester **13a**, which could be due to the leaving ability of the attached cyclopenetenedione moiety. The other two products were determined to be geometrical isomers of 5-[(*tert*-butoxycarbonyl)methylene]-2(5*H*)-furanone **14a** (*E*/*Z* = 73/27) by comparison with the authentic (*E*)- and (*Z*)-isomers (31/69) which were obtained by our established procedure using $Pb(OAc)_4$ oxidation (i.e., via an intermediate such as **9**).[5c] In this case, the stereochemistry could be determined based on the relative ^{1}H NMR chemical shift due to an *exo*-methylene proton, which was observed at a lower region in *E* (δ 5.85) than in *Z* (δ 5.54).[5c,9] This tendency was used to deduce the stereochemistry of analogous products obtained from **12b**,**c**. Other Lewis acids such as $TiCl_4$ and $SnCl_4$ resulted in negligible yields of **13d** (entries 2 and 3). On the other hand, trifluoroacetic acid (TFA) catalyzed ring expansion with much better yields [**13d**: 50%, **14a**: 23% (*E*/*Z* = 58/42)] under the same reaction conditions (entry 4); similar results were obtained in the case of trimethylsilyl triflate (TMSOTf) (entry 5). Carbene-type rearrangement was achieved by catalysis with $Rh_2(OAc)_4$ and by photolysis (entries 6 and 7). While these "lyses" may proceed via different mechanisms, the same products were obtained in the selective formation of the cyclopentenedione (**13d**: 77%, **14a**: 6% for Rh-catalysis; **13d**: 45%, **14a**: 14% for photolysis).

Among the reaction conditions examined above, the catalytic reactions using TFA, TMSOTf, and $Rh_2(OAc)_4$ were fruitful and therefore selected for diazo-ester **12b** and diazo-ketone **12c**. In the same manner, corresponding products **13b**,**c** and **14b**,**c** were obtained in comparable yields, as shown in entries 8−13, and were characterized by analogy with **13d** and **14a**. The TFA-catalyzed reaction selectively gave the furanone **14b** from **12b** and the cyclopentenedione **13c** from **12c**. The cyclopentenedione structure of **13b** from the ethyl ester **12b** was very susceptible to fragmentation, as seen in the *tert*-butyl ester **13a**, and thus Rh-catalyzed decomposition was accompanied by the minor formation of **13d**.

The relative yields of cyclopentenedione to furanone (**13**/**14**) shown in Table 1 seem to reflect a kinetic product ratio, except for the less significant reactions in entries

Table 1. Catalyzed and Photolyzed Reaction of Diazo-Functionalized Cyclobutenones 12a−c



12a-c **13a-d** **14a-c**

a R = COO^{t}Bu, **b** R = COOEt, **c** R=COPh, **d** R = H

entry	compd	catalyst[a] [amount]	temp,[b] °C	product [yield (%)] (*E*/*Z* ratio)[c]	
1	**12a**	BF_3 [1.2 equiv]	0	**13d** [9],	**14a** [27] (*E*/*Z* = 73/27)
2	**12a**	$TiCl_4$ [1.2 equiv]	0	**13d** [18]	
3	**12a**	SnCl [1.2 equiv]	0	**13d** [2]	
4	**12a**	TFA [1.2 equiv]	0	**13d** [50],	**14a** [23] (*E*/*Z* = 58/42)
5	**12a**	TMSOTf [20 mol %]	rt	**13d** [42],	**14a** [36] (*E*/*Z* = 73/27)
6	**12a**	$Rh_2(OAc)_4$ [2.5 mol %]	0	**13d** [77],	**14a** [6] (*E*/*Z* = 0/100)
7	**12a**	*hν*	rt	**13d** [45],	**14a** [14] (*E*/*Z* = 75/25)
8	**12b**	TFA [1.2 equiv]	0		**14b** [51] (*E*/*Z* = 50/50)
9	**12b**	TMSOTf [20 mol %]	rt		**14b** [58] (*E*/*Z* = 75/25)
10	**12b**	$Rh_2(OAc)_4$ [2.5 mol %]	0	**13b** [69]/**13d** [17]	
11	**12c**	TFA [1.2 equiv]	0	**13c** [83]	
12	**12c**	TMSOTf [20 mol %]	rt	**13c** [50],	**14c** [47] (*E*/*Z* = 64/36)
13	**12c**	$Rh_2(OAc)_4$ [2.5 mol %]	0	**13c** [70]	

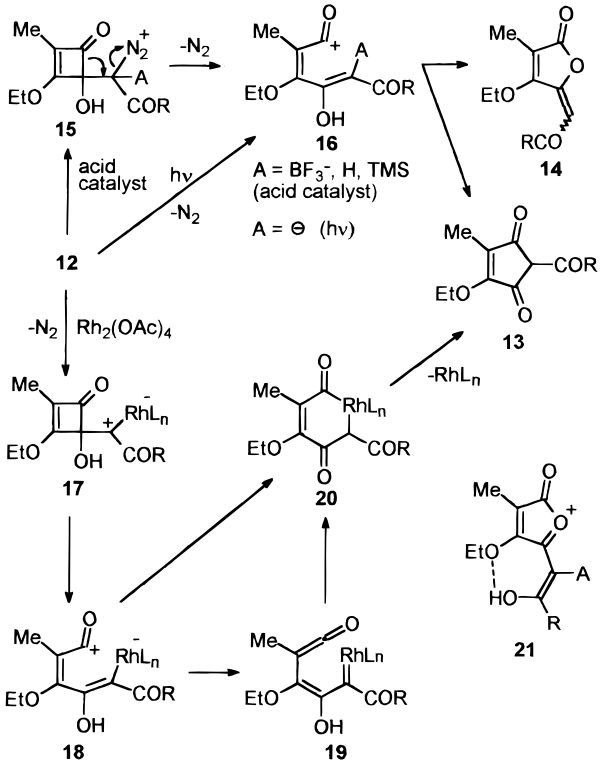
[a] Solvent CH_2Cl_2. [b] Reaction time: 30 min except for entry 7 (19 h). [c] The ratio was obtained by ^{1}H NMR measurement.

(7) Squarate **2** was not suitable since the nucleophilic addition did not occur at −78 °C. Furthermore, α-diazo carbonyl compounds were used since derivatives of diazoalkane such as (trimethylsilyl)diazomethane were too unstable [decomposition during workup gave only 12% of the cyclopentenedione (**13**: R = TMS) as a product].

(8) Pellicciari, R.; Natalini, B.; Sadeghpour, B. M.; Marinozzi, M.; Snyder, J. P.; Williamson, B. L.; Kuethe, J. T.; Padwa, A. *J. Am. Chem. Soc.* **1996**, *118*, 1. References are listed for some reactions of α-diazo *β*-hydroxy carbonyl compounds.

(9) Begley, M. L.; Gedge, D. R.; Pattenden, G. *J. Chem. Soc., Chem. Commun.* **1978**, 60.

Scheme 4



1−3. Control experiments indicated that **13** and **14** were not interconvertible under these conditions[10] (the possibility of the conversion **13a** to **14a** can be excluded because of concomitant fragmentation). The observed difference in the product ratio may be explained by the nature of the catalysts and the enolizability of the intermediates involved (vide infra). The *E*/*Z* ratio of the furanones **14** varied slightly depending on the reaction conditions, although (*E*)-isomers were generally predominant (*E*/*Z* ∼ 7/3).[11]

The mechanism of the ring expansion to two types of five-membered rings is illustrated in Scheme 4. Regardless of the catalysts used, these rearrangements can be explained by considering the participation of an electron-deficient carbon center, which is generated by the action of the catalysts or by photoexcitation and triggers the ring expansion of cyclobutenone. Padwa's related rearrangement of 2-diazo-(1-hydroxycyclobutyl)acetate has been suggested to proceed via (1) complexation of the alcohol functionality with a BF_3 catalyst to generate cyclobutylidene diazonium salt, (2) loss of nitrogen to produce a linear vinyl cation, and (3) a 1,2-methylene shift to a cyclopentenyl cation (see Scheme 3).[8] However, this mechanism is not consistent with our experimental findings, since the furanone, one of the ring-expansion products, should originate from the ring-opened structure. Our previous ring-expansion reaction induced by an α-vinyl cation (i.e., **7** → **8**) proceeded via the formation of ring-opened acyl cation and recombination with an allenyl end.[5f] In the analogous TFA-catalyzed rearrangement of succinoin derivatives, a similar process (recombination of the acyl cation with an enol end) was reported to be likely.[12] These sequential reaction paths are consistent with the formation of both products from the catalytic and photolytic reactions as described above. Thus, protonation (silylation) or coordination of BF_3 on the diazo group produces a diazonium salt **15**, which then eliminates nitrogen to generate a carbocation α to the cyclobutenone ring. Interaction of the Rh catalyst with this group forms a Rh−carbene complex **17**, which has a positive center because of the polar nature of the metal−carbon double bond.[13] The carbene generated under photolytic conditions can be considered an electropositive intermediate.[14] Therefore, these intermediates with an electron-deficient center, while formed by different processes, induce ring-opening to give stable conjugated acyl cations **16**. In the subsequent recyclization step, these cations have two opportunities to form a new bond with both oxygen and carbon sites of the opposite enol end, giving **13** and **14**, respectively. In contrast, all of the Rh-catalyzed reactions produced the cyclopentenedione selectively. Since the Rh−carbenoid is known to undergo cation-like rearrangement,[15] **17** can also follow the similar type of ring-opening to give a zwitterionic intermediate **18**. While simple recyclization of **18** might lead to the formation of **13**, we prefer the involvement of a metallacyclic intermediate **20** formed either from the direct recombination of an acyl cation with a Rh center or from the 6π electrocyclization of a conjugated vinylketene **19**. Subsequent reductive elimination may be responsible for the observed selectivity.[16] It is difficult to completely explain the selectivity observed in TFA- and TMSOTf-catalyzed reactions; e.g., TFA selectively produces the furanone in **12b**, the cyclopentenedione in **12c**, and both in **12a**, whereas TMSOTf tends to enhance furanone formation. Nevertheless, the preference for an enol form in the ring-opened 1,3-dicarbonyl intermediate **16** might be due to C−C bond formation rather than C−O bond formation. On the other hand, a bulky silyl group may play a role in TMSOTf catalysis, thus retarding the formation of the former bond. Finally, we consider the stereochemistry of the furanone products. While the oxy-radical-mediated reaction predominantly gave the thermodynamically favored (*Z*)-isomer (**3** → **10b**),[5c] content of (*E*)-isomer was increased in the present reaction.[17] A hydrogen-bonded structure such as **21** might contribute in part to this inverse trend at the recyclization step.

The thermal reaction of diazo-functionalized cyclobutenones **12** is a new type of ring transformation based on **1**. In contrast to the above decomposition reactions, the

(10) Base-promoted conversion of 5-acylidene-2(5*H*)-furanone to 2-acyl-4-cyclopentene-1,3-dione has been reported: Gedge, D. R.; Pattenden, G. *J. Chem. Soc., Chem. Commun.* **1978**, 880.

(11) Control experiments suggested that the acid-catalyzed conditions had little effect on the geometrical isomerization of formed furanones **14**.

(12) Shimada, J.; Hashimoto, K.; Kim, B. H.; Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1984**, *106*, 1759.

(13) Ohno, M.; Itoh, M.; Umeda, M.; Furuta, R.; Kondo, K.; Eguchi, S. *J. Am. Chem. Soc.* **1996**, *118*, 7075. See ref 6d for the case of chromium carbene complexes.

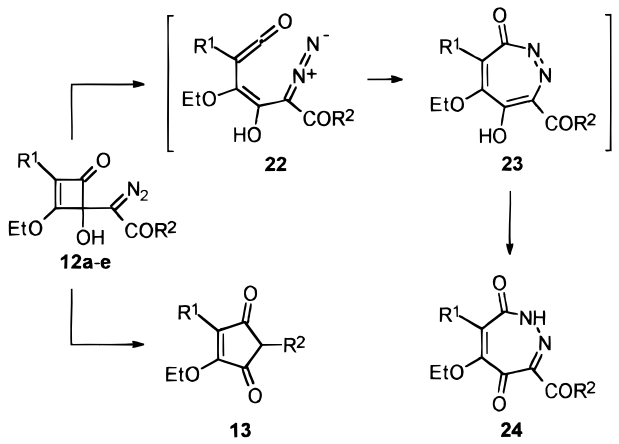
(14) The rearrangement of cyclobutylcarbene to cyclopentene has been reported: Paskovich, D. H.; Kwok, P. W. N. *Tetrahedron Lett.* **1967**, 2227. For a general discussion on 1,2-rearrangement of carbene, see Nickon, A. *Acc. Chem. Res.* **1993**, *26*, 84, and refs cited therein.

(15) For example, we have previously observed adamantylmethyl−homoadamantyl rearrangement (which is typical in the cationic version) in the reaction of adamantyldiazoacetate with $Rh_2(OAc)_4$; see ref 13.

(16) Zwitterionic intermediates have often been proposed in the Rh-promoted carbene rearrangement, in which a metallacycle is postulated as a plausible intermediate: (a) Padwa, A.; Austin, D. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1797. (b) Müller, P.; Pautex, N.; Doyle, A. P.; Bagheri, V. *Helv. Chim. Acta* **1990**, *73*, 1233.

(17) In an exception, the (*Z*)-isomer was a minor product in the Rh-catalysis of **12a** (entry 6), probably because of coordination with a Rh center.

Scheme 5



	R1	R2	Yield		R1	R2	Yield
				a	Me	O ^{t}Bu	56 %
				b	Me	OEt	46 %
c	Me	COPh	42 %	**c**	Me	Ph	24 %
e	Bu	H	16 %	**d**	Bu	O ^{t}Bu	44 %
f	Ph	H	46 %				

products were obtained as structural isomers in moderate yields, when **12a**−**c** were heated to reflux in xylene for 30 min. This isomerism was revealed by an MS analysis, which showed molecular ion peaks with the same mass numbers (*m*/*z* 254 and 286) as those of starting **12b** and **12c**, respectively, and was also supported by an elemental analysis. The presence of an amino group was indicated by IR absorption at around 3200 cm^{-1}. The ^1H NMR spectra contained a broad singlet due to a NH group (δ 9.39−9.73), and all of the ^{13}C NMR signals due to skeletal carbons appeared in the sp^2 region. These data allowed us to assign the products as diazepinediones **24a**−**c**, which is consistent with the mechanism described below. Although photolysis facilitated the decomposition of a diazo group, it remained intact during thermolysis to lead to a diazovinylketene intermediate **22** via 4π electrocyclic ring-opening. The resulting conjugated system **22** could recyclize via 8π electrocyclic ring closure (1,7-dipolar cyclization) to **23**, which was followed by prototropy to the diazepinedione **24** (Scheme 5). 8π Electrocyclization is a useful method for the synthesis of 1,2-diazepine.[18] The reaction of **12c** was accompanied by the formation of **13c** via the aforementioned carbene route; similarly, **12d** gave both **13e** and **22d**. Phenyl-substituted **12e** resulted in the formation of only **13f**. Since the 2-substituent on **12** influences the 4π electrocyclic ring-opening less significantly,[2] the relative instability of the diazo group led to the carbene route.

In summary, diazo-functionalized 4-hydroxycyclobutenones **12** derived from **1** underwent ring-expansion to cyclopentenedione/2(5*H*)-furanone **13**/**14** through a sequential ring-opening and recombination process, triggered by an electron-deficient carbon center generated upon catalysis and photolysis. The thermal reaction of **12** gave a new seven-membered heterocyclic ring system, diazepinedione **22**, via tandem 4π−8π electrocyclic ring opening−closure as a new type of ring transformation in squaric acid chemistry.[19]

Experimental Section

General Remarks. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ solution with $SiMe_4$ as an internal standard. CH_2Cl_2 was dried over $CaCl_2$, distilled, and kept over 4 Å molecular sieves, while THF was dried over Na/Ph_2CO and distilled before use. Aromatic solvents were dried over Na. Flash chromatography was carried out using a Fuji-Davison BW-300 with hexane (H) and ethyl acetate (A) as an eluent. Squaric acid was provided by Kyowa Hakko Kogyo Co., Ltd. Preparation of the squaric acid derivatives **11a**−**c** has been reported previously.[3c,20]

Representative Procedure for the Synthesis of 12a−**e.** To a solution of **11a** (1117 mg, 7.97 mmol) and *tert*-butyl diazoacetate (2266 mg, 15.94 mmol) in THF (40 mL) was added LDA [prepared from diisopropylamine (1937 mg, 19.14 mmol) and BuLi (11.86 mL of 1.6 M hexane solution, 19.14 mmol) and cooled at −10 °C] at −78 °C under a nitrogen atmosphere, and the solution was stirred for 1 h at this temperature. After the solution was mixed with 1 N HCl (10 mL) and diluted with brine, the product was extracted with ether (50 mL × 3). Extracts were washed with brine, dried over Na_2SO_4, and evaporated to dryness. The residue was chromatographed to give the diazocyclobutenone **12a** (868 mg, 47%).

In the same manner, **12d** and **12e** were obtained in yields of 41% and 46% from **11b** and **11c**, respectively. Furthermore, **12b** and **12c** were obtained in yields of 41% and 30% from **11a** with ethyl diazoacetate and benzoyldiazomethane, respectively, except that the reaction was for 2 h at −78 °C and quenching was with aq NH_4Cl for **12b** and acetic acid for **12c**.

***tert*-Butyl 2-(2-ethoxy-1-hydroxy-3-methyl-4-oxo-2-cyclobutenyl)-2-diazoacetate (12a):** Elution with (H/A 3/1); oil; IR (neat) 2103, 1761, 1694, 1616 cm^{-1}; ^1H NMR δ 1.46 (3 H, t, J = 7.0 Hz), 1.47 (9 H, s), 1.72 (3 H, s), 4.41 and 4.51 (each 1 H, dq, J = 9.9, 7.0 Hz), 5.15 (1 H, br s); ^{13}C NMR δ 6.8, 15.2, 28.4 (3C), 31.3, 69.2, 82.9, 85.9, 125.2, 165.5, 181.9, 189.9; MS (EI) *m*/*z* (relative intensity), 199 (M − 83, 14), 152 (87), 83 (100). Anal. Calcd for $C_{13}H_{18}N_2O_5$: C, 55.31; H, 6.43; N, 9.22. Found: C, 55.86; H, 6.10; N, 9.42.

Ethyl 2-(2-ethoxy-1-hydroxy-3-methyl-4-oxo-2-cyclobutenyl)-2-diazoacetate (12b): Elution with (H/A 5/1); crystal, mp 81−83 °C; IR (KBr) 2103, 1763, 1696, 1615 cm^{-1}; ^1H NMR δ 1.26 (3 H, t, J = 7.2 Hz), 1.46 (3 H, t, J = 7.0 Hz), 1.72 (3 H, s), 4.21 (2 H, q, J = 7.0 Hz), 4.42 and 4.52 (each 1 H, dq, J = 9.8, 7.0 Hz), 5.51 (1 H, br s); ^{13}C NMR δ 6.7, 14.4, 15.1, 58.2, 61.2, 69.2, 85.3, 125.1, 165.4, 182.3, 190.7; MS (EI) *m*/*z* (relative intensity), 226 (M − 28, 5), 152 (51), 83 (100). Anal. Calcd for $C_{11}H_{14}N_2O_5$: C, 51.97; H, 5.55; N, 11.02. Found: C, 52.13; H, 5.57; N, 10.84.

4-(1-Diazo-2-oxo-2-phenylethyl)-3-ethoxy-4-hydroxy-2-methyl-2-cyclobutenone (12c): Elution with (H/A 3/1); oil; IR (neat) 2091, 1763, 1615, 708 cm^{-1}; ^1H NMR δ 1.48 (3 H, t, J = 7.0 Hz), 1.79 (3 H, s), 4.45 and 4.56 (each 1 H, dq, J = 9.8, 7.0 Hz), 5.77 (1 H, br s), 7.40−7.65 (5 H, m); ^{13}C NMR δ 6.9, 15.1, 67.8, 69.4, 86.6, 125.5, 127.6 (2C), 129.1 (2C), 132.5, 137.3, 181.8, 189.5, 189.6; MS (EI) *m*/*z* (relative intensity), 258 (M − 28, 38), 105 (100). Anal. Calcd for $C_{15}H_{14}N_2O_4$: C, 62.93; H, 4.93; N, 9.79. Found: C, 62.78; H, 5.00; N, 9.71

***tert*-Butyl 2-(3-butyl-2-ethoxy-1-hydroxy-4-oxo-2-cyclobutenyl)-2-diazoacetate (12d):** Elution with (H/A 5/1); oil; IR (neat) 2101, 1755, 1694, 1609 cm^{-1}; ^1H NMR δ 0.90 (3 H, t, J = 7.2 Hz), 1.23−1.60 (4 H, m), 1.45 (3 H, t, J = 7.0 Hz), 1.47 (9 H, s), 2.11 (2 H, t, J = 7.4 Hz), 4.38 and 4.51 (each 1 H, dq, J = 9.9, 7.0 Hz), 5.40 (1 H, br s); ^{13}C NMR δ 13.7, 15.2,

(18) (a) Sharp, J. T. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: Oxford, 1984; Vol. 7, pp 595−604. (b) For an example of 6π electrocyclization of diazoketene, see Tomioka, H.; Okuno, A.; Sugiyama, T.; Murata, S. *J. Org. Chem.* **1995**, *60*, 2344.

(19) For a previous ring transformation based on **1** to a seven-membered ring, see: Huffman, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 4895.

(20) For the synthesis of these types of compounds from **1**, see (a) Reed, M. W.; Polart, D. J.; Perri, S. T.; Foland, L. D.; Moore, H. W. *J. Org. Chem.* **1988**, *53*, 2477. (b) Liebeskind, L. S.; Fengl, R. W.; Wirtz, K. R.; Shawe, T. T. *J. Org. Chem.* **1988**, *53*, 2482.

22.1, 22.6, 28.4 (3C), 31.3, 69.0, 83.0, 85.9, 130.1, 165.5, 181.8, 189.6; MS (EI) *m/z* (relative intensity), 240 (M − 84, 34), 151 (100). Anal. Calcd for $C_{16}H_{24}N_2O_5$: C, 59.24; H, 7.46; N, 8.64. Found: C, 59.43; H, 7.45; N, 8.46.

***tert*-Butyl 2-(2-ethoxy-1-hydroxy-3-phenyl-4-oxo-2-cyclobutenyl)-2-diazoacetate (12e):** Elution with (H/A 10/1); crystal, mp 127−129 °C; IR (KBr) 2105, 1742, 1692, 1622 cm^{-1}; ^1H NMR δ 1.39 (9 H, s), 1.55 (3 H, t, J = 7.2 Hz), 4.52 and 4.70 (each 1 H, dq, J = 9.8, 7.0 Hz), 5.73 (1 H, br s), 7.25−7.73 (5 H, m); ^{13}C NMR δ 15.2, 28.4 (3C), 31.2, 69.0, 70.0, 83.0, 86.6, 126.3, 127.6 (2C), 128.7, 128.6, 128.7, 128.8 (2C), 165.5, 180.9, 187.9; MS (EI) *m/z* (relative intensity), 316 (M − 28, 34), 242 (52), 214 (100). Anal. Calcd for $C_{18}H_{20}N_2O_5$: C, 62.78; H, 5.85; N, 8.13. Found: C, 62.89; H, 6.02; N, 7.85.

Representative Procedure for the Catalyzed Decomposition of 12a−c. To a solution of **12a** (116 mg, 0.41 mmol) in CH_2Cl_2 (2 mL) was added a catalyst in the amount and at the temperature shown in Table 1 under a nitrogen atmosphere, and stirring was continued for 30 min. The solution was then mixed with 10% aq $NaHCO_3$ (5 mL), and the products were extracted with ether (10 mL × 3). The combined extracts were washed with brine, dried over Na_2SO_4, and evaporated to dryness. The residue was chromatographed to give the cyclopentenedione and/or furanone. The yields are summarized in Table 1.

4-Ethoxy-5-methyl-4-cyclopentene-1,3-dione (13d): Elution with H/A 10/1; oil as the first fraction; IR (neat) 1755, 1696, 1622 cm^{-1}; ^1H NMR δ 1.40 (3 H, t, J = 7.0 Hz), 1.94 (3 H, t, J = 1.0 Hz), 2.91 (2 H, q, J = 1.0 Hz), 4.69 (2 H, q, J = 7.0 Hz); ^{13}C NMR δ 7.2, 15.9, 42.2, 68.1, 137.4, 166.7, 196.0, 197.2; MS (EI) *m/z* (relative intensity), 154 (M^+, 52), 83 (100). Anal. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54. Found: C, 62.45; H, 6.42.

(*E*)-5-[(*tert*-Butoxycarbonyl)methylidene]-4-ethoxy-3-methyl-2(5*H*)-furanone ((*E*)-14a): Elution with H/A 10/1; oil as the second fraction; IR (neat) 1780, 1726, 1638 cm^{-1}; ^1H NMR δ 1.41 (3 H, t, J = 7.0 Hz), 1.51 (9 H, s), 2.07 (3 H, s), 4.45 (2 H, q, J = 7.0 Hz), 5.85 (1 H, s); ^{13}C NMR δ 9.1, 15.3, 28.2 (3C), 68.3, 82.3, 103.4, 103.9, 149.4, 161.3, 163.5, 170.3; MS (EI) *m/z* (relative intensity), 254 (M^+, 2), 199 (77), 181 (100). Anal. Calcd for $C_{13}H_{18}O_5$: C, 61.40; H, 7.13. Found: C, 61.35; H, 7.18.

***(Z)*-5-[(*tert*-Butoxycarbonyl)methylidene]-4-ethoxy-3-methyl-2(5*H*)-furanone ((*Z*)-14a):** Elution with H/A 10/1; crystal as the third fraction, mp 108−111 °C; IR (KBr) 1782, 1717, 1680, 1647 cm^{-1}; ^1H NMR δ 1.42 (3 H, t, J = 7.0 Hz), 1.51 (9 H, s), 2.08 (3 H, s), 4.46 (2 H, q, J = 7.0 Hz), 5.54 (1 H, s); ^{13}C NMR δ 8.9, 15.3, 28.2 (3C), 67.9, 81.7, 97.4, 101.6, 152.3, 161.8, 163.4, 170.2; MS (EI) *m/z* (relative intensity), 254 (M^+, 2), 199 (76), 181 (100). Anal. Calcd for $C_{13}H_{18}O_5$: C, 61.40; H, 7.13. Found: C, 61.45; H, 7.08.

Ethyl 3-ethoxy-4-methyl-2,5-dioxo-3-cyclopentenecarboxylate (13b): Elution with H/A 10/1, oil as the first fraction; IR (neat) 1759, 1723, 1696, 1622 cm^{-1}; ^1H NMR δ 1.28 (3 H, t, J = 7.2 Hz), 1.41 (3 H, t, J = 7.0 Hz), 1.98 (3 H, t, J = 0.8 Hz), 3.83 (1 H, q, J = 0.8 Hz), 4.23 (2 H, q, J = 7.2 Hz), 4.74 (2 H, q, J = 7.0 Hz); ^{13}C NMR δ 7.5, 14.0, 15.8, 58.2, 62.6, 68.6, 138.7, 165.0, 167.6, 190.8, 191.8; MS (EI) *m/z* (relative intensity), 226 (M^+, 24), 198 (100). Anal. Calcd for $C_{11}H_{14}O_5$: C, 58.35; H, 6.24. Found: C, 58.28; H, 6.31.

(*E*)- and (*Z*)-5-[(Ethoxycarbonyl)methylidene]-4-ethoxy-3-methyl-2(5*H*)-furanone ((*E*)- and (*Z*)-14b). These compounds were obtained as an inseparable mixture on elution with H/A 10/1; oil as the second fraction; IR (neat) 1780, 1726, 1638 cm^{-1}; ^1H NMR (chemical shifts due to the *Z*-isomer are indicated in brackets) δ 1.32 [1.32] (3 H, t, J = 7.0 Hz), 1.41 [1.43] (3 H, t, J = 7.0 Hz), 1.51 (9 H, s), 2.08 [2.09] (3 H, s), 4.23 [4.26] (2 H, q, J = 7.0 Hz), 4.45 [4.48] (2 H, q, J = 7.0 Hz), 5.89 [5.61] (1 H, s); ^{13}C NMR δ 9.0 [8.9], 14.1 [14.3], 15.1 [15.2], 61.4 [61.0], 68.3 [68.0], 101.7 [95.6], 104.2 [101.8], 150.4 [152.9], 161.1 [161.7], 164.6 [164.1], 170.0 [170.1]; MS (EI) *m/z* (relative intensity), 226 (M^+, 12), 198 (95), 83 (100). Anal. Calcd for $C_{11}H_{14}O_5$: C, 58.35; H, 6.24. Found: C, 58.37; H, 6.22.

2-Benzoyl-4-ethoxy-5-methyl-4-cyclopentene-1,3-dione (13c): Elution with H/A 6/1; oil as the first fraction; IR (neat) 1715, 1699, 1624 cm^{-1}; ^1H NMR δ 1.40 (3 H, t, J = 7.0 Hz), 1.98 (3 H, s), 4.67 (2 H, q, J = 7.0 Hz), 7.43−7.99 (5 H, m), 13.7 (1 H, br s); ^{13}C NMR δ 6.5, 15.8, 68.1, 123.9, 128.3 (2C), 129.9 (2C), 130.2, 132.9, 163.8, 171.8, 185.4, 196.9, 201.0; MS (EI) *m/z* (relative intensity), 258 (M^+, 71), 105 (100). Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 69.88; H, 5.34.

(*E*)-5-(Benzoylmethylidene)-4-ethoxy-3-methyl-2(5*H*)-furanone ((*E*)-14c): Elution with H/A 6/1; crystal as the third fraction, mp 118−120 °C; IR (KBr) 1784, 1682, 1645, 1622 cm^{-1}; ^1H NMR δ 1.49 (3 H, t, J = 7.0 Hz), 2.11 (3 H, s), 4.53 (2 H, q, J = 7.0 Hz), 6.50 (1 H, s); 7.44−7.99 (5 H, m); ^{13}C NMR δ 9.0, 15.4, 68.1, 99.5, 101.9, 129.0 (4C), 133.6, 138.4, 151.9, 161.9, 170.4, 189.1; MS (EI) *m/z* (relative intensity), 258 (M^+, 10), 105 (100). Anal. Calcd for $C_{15}H_{11}O_4$: C, 69.76; H, 5.46. Found: C, 69.79; H, 5.43.

(*Z*)-5-(Benzoylmethylidene)-4-ethoxy-3-methyl-2(5*H*)-furanone ((*Z*)-14c): Elution with H/A 6/1; crystal as the second fraction, mp 120−122 °C; IR (KBr) 1792, 1669, 1653, 1636 cm^{-1}; ^1H NMR δ 0.91 (3 H, t, J = 7.0 Hz), 2.03 (3 H, s), 4.18 (2 H, q, J = 7.0 Hz), 6.34 (1 H, s); 7.44−8.00 (5 H, m); ^{13}C NMR δ 8.9, 14.4, 68.1, 103.3, 107.4, 129.0 (2C), 129.5 (2C), 134.0, 138.0, 148.7, 161.1, 170.4, 191.6; MS (EI) *m/z* (relative intensity), 258 (M^+, 7), 105 (100). Anal. Calcd for $C_{15}H_{11}O_4$: C, 69.76; H, 5.46. Found: C, 69.78; H, 5.44.

Photolysis of 12a. A solution of **12a** (200 mg, 0.708 mmol) in CH_2Cl_2 (5 mL) was irradiated with a 100-W high-pressure Hg lamp with a Pyrex glass filter for 19 h at ambient temperature under a nitrogen atmosphere. After evaporation of the solvent, the products were separated by the method that was used for the catalyzed reaction (see Table 1 for the yields).

Independent Synthesis of (*E*)- and (*Z*)-Furanone 14a. To a solution of **11a** (237 mg, 1.69 mmol) in THF (12 mL) was added a THF solution (3 mL) of lithium enolate of *tert*-butyl acetate [prepared from this ester (236 mg, 2.03 mmol) and LDA (diisopropylamine + 1.6 M hexane solution of BuLi, each 2.03 mmol), −10 °C, 30 min] at −78 °C under a nitrogen atmosphere, and stirring was continued for 30 min. After the solution was mixed with 5% aq NH_4Cl (10 mL), the products were extracted with ether (10 mL × 3). The extracts were combined, washed with brine, dried over Na_2SO_4, and evaporated to dryness. The residue was chromatographed (H/A 3/1) to give *tert*-butyl 2-ethoxy-1-hydroxy-3-methyl-4-oxo-2-cyclobutenylacetate (248 mg, 57%): crystal, mp 80−83 °C; IR (neat) 1748, 1723, 1603 cm^{-1}; ^1H NMR δ 1.45 (3 H, t, J = 7.0 Hz), 1.48 (9 H, s), 1.74 (3 H, s), 2.69 and 2.77 (each 1 H, d, J = 15.4 Hz), 4.40 and 4.50 (2 H, dq, J = 9.8, 7.0 Hz), 4.68 (1 H, br s); ^{13}C NMR δ 7.0, 15.1, 28.1 (3C), 38.3, 68.9, 82.7, 88.3, 122.2, 171.3, 181.8, 191.1; MS (EI) *m/z* (relative intensity), 200 (M^+ − 57, 70), 155 (100). Anal. Calcd for $C_{13}H_{20}O_5$: C, 60.92; H, 7.86. Found: C, 60.97; H, 7.81.

The above cyclobutenylacetate (197 mg, 0.77 mmol) was dissolved in benzene (5 mL) and added to a solution of $Pb(OAc)_4$ (682 mg, 1.54 mmol) in benzene (5 mL) at room temperature under a nitrogen atmosphere, and stirring was continued for 30 min. The reaction mixture was then treated with water (10 mL) and the precipitates were removed by filtration. The products were extracted with ether (15 mL × 3), and the extracts were washed with brine, dried over Na_2SO_4, and evaporated to dryness. The residue was chromatographed (H/A 10/1) to give (*E*)-**14a** (15 mg, 8% as the first fraction) and (*Z*)-**14a** (36 mg, 18% as the second fraction) together with 5-acetoxy-5-[(*tert*-butoxycarbonyl)methyl]-4-ethoxy-3-methyl-2(5*H*)-furanone (145 mg, 60% as the third fraction).

Representative Procedure for the Thermal Ring Expansion of 12a−e. A solution of **12a** (70 mg, 0.25 mmol) in *p*-xylene (10 mL) was heated to reflux for 2 h under a nitrogen atmosphere. After evaporation of the solvent, the residue was chromatographed (H/A 10/1) to give the diazepinedione **22a** (39 mg, 56%).

Compounds **12b−e** were treated similarly, and the products were separated. The yields are shown in Scheme 4; the cyclopentenediones **13d**,**e** have been reported previously.[5c]

***tert*-Butyl 5-ethoxy-6-methyl-4,7-dioxo-1,2(1*H*)-diazepine-3-carboxylate (24a):** crystal, mp 99−103 °C; IR (KBr) 3187, 1715, 1698, 1644 cm^{-1}; ^1H NMR δ 1.37 (3 H, t, J = 7.0 Hz), 1.55 (9 H, s), 2.16 (3 H, s), 4.22 (2 H, q, J = 7.0 Hz), 9.39 (1 H, br s); ^{13}C NMR δ 13.7, 15.5, 28.0 (3C), 67.9, 84.5, 125.1, 141.2, 160.7, 161.9, 166.8, 180.1; MS (EI) *m*/*z* (relative intensity), 226 (M^+ − 56, 29), 152 (52), 83 (100). Anal. Calcd for $C_{13}H_{18}N_2O_5$: C, 55.31; H, 6.43; N, 9.92. Found: C, 55.45; H, 6.43; N, 9.78.

Ethyl 5-ethoxy-6-methyl-4,7-dioxo-1,2(1*H*)-diazepine-3-carboxylate (24b): crystal, mp 96−98 °C; IR (KBr) 3183, 1723, 1680, 1645 cm^{-1}; ^1H NMR δ 1.37 (3 H, t, J = 7.2 Hz), 1.38 (3 H, t, J = 7.0 Hz), 2.17 (3 H, s), 4.24 (2 H, q, J = 7.0 Hz), 4.40 (2 H, q, J = 7.0 Hz), 9.70 (1 H, br s); ^{13}C NMR δ 13.8, 14.1, 15.4, 62.9, 68.1, 125.2, 139.6, 160.7, 162.9, 166.8, 179.6; MS (EI) *m*/*z* (relative intensity), 254 (M^+, 12), 152 (41), 83 (100). Anal. Calcd for $C_{13}H_{18}N_2O_5$: C, 55.31; H, 6.43; N, 9.92. Found: C, 55.45; H, 6.43; N, 9.78.

3-Benzoyl-5-ethoxy-6-methyl-1,2(1*H*)-diazepine-4,7-dione (24c): paste as the second fraction after the first fraction of **13c** by chromatography; IR (neat) 3277, 1665, 1630 cm^{-1}; ^1H NMR δ 1.40 (3 H, t, J = 7.0 Hz), 2.21 (3 H, s), 4.27 (2 H, q, J = 7.0 Hz), 7.45−7.98 (5 H, m), 9.50 (1 H, br s); ^{13}C NMR δ 14.1, 15.5, 68.5, 126.6, 128.9 (2C), 130.5 (2C), 134.4, 135.7, 145.1, 161.1, 166.8, 181.3, 191.5; MS (EI) *m*/*z* (relative intensity), 286 (M^+, 3), 105 (100). Anal. Calcd for $C_{15}H_{14}N_2O_4$: C, 62.93; H, 4.93; N, 9.79. Found: C, 63.10; H, 4.99; N, 9.56.

***tert*-Butyl 6-butyl-5-ethoxy-4,7-dioxo-1,2(1*H*)-diazepine-3-carboxylate (24d):** crystal as the second fraction after the first fraction of **13d** by chromatography, mp 81−83 °C; IR (KBr) 3239, 1726, 1682, 1657 cm^{-1}; ^1H NMR δ 0.94 (3 H, t, J = 7.0 Hz), 1.35−1.51 (4 H, m), 1.36 (3 H, t, J = 7.0 Hz), 1.56 (9 H, s), 2.64 (2 H, q, J = 7.4 Hz), 4.19 (2 H, q, J = 7.0 Hz), 9.55 (1 H, br s); ^{13}C NMR δ 14.0, 15.5, 23.0, 27.5, 28.1 (3C), 30.4, 67.9, 84.5, 129.2, 141.0, 160.7, 162.0, 166.8, 180.6; MS (EI) *m*/*z* (relative intensity), 324 (M^+, 7), 195 (100), 151 (85). Anal. Calcd for $C_{16}H_{24}N_2O_5$: C, 59.24; H, 7.46; N, 8.64. Found: C, 59.33; H, 7.51; N, 8.50.

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